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(21) International Application Number: PCT/EP94/03541 (22) International Filing Date: 27 October 1994 (27.10.94) (30) Priority Data: 145,873 2 November 1993 (02.11.93) US 306,071 19 September 1994 (19.09.94) US (71) Applicant (for all designated States except US): GIVAUDAN-ROURE (INTERNATIONAL) S.A. [CH/CH]; 5, chemin de la Parfumerie, CH-1214 Vernier (CH). (72) Inventors; and (75) Inventors/Applicants (for US only): McGEE, Thomas [GB/US]; 5 Kingswood Drive, Orangeburg, NY 10962 (US). SUBRAMANIAN, Saroja [IN/US]; Apartment 19, 59 Paulison Avenue, Passaic, NJ 077055 (US). YEAGER, Caryl, E. [US/US]; 23 Crestview Avenue, Madison, NJ 07940 (US). (74) Agent: URECH, Peter; P.O. Box 3255, CH-4002 Basle (CH).		(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PERFUME FORMULATIONS (57) Abstract <p>Oil-in-water (O/W) and water-in-oil (W/O) microemulsions of fragrance product formulations are provided. The microemulsions are clear or at least translucent, sprayable, and nonsticky. Novel combinations of anionic surfactant components (a) and hydrophilic coactives (highly water soluble component (b) or a mixture of highly water soluble (b)(i) and less water soluble polar (b)(ii) components) are used to obtain fragrance product formulations that are free or substantially free of ethanol. The anionic surfactants have a hydrophilic-lipophilic balance ("HLB") modified by the use of classes of anionic surfactant components (a) and commercially available hydrophilic component coactives ((b) or mixture of (b)(i) and (b)(ii)), not previously recognized as effective in this type of system. Highly, preferably infinitely, water soluble coactives (b) as well as mixtures of highly, preferably infinitely, water soluble coactives (b)(i) with other less water soluble polar coactives (b)(ii), modify the HLB of anionic surfactants in such a way as to enable the formation of stable, clear microemulsions of fragrance product compositions. These compositions contain lower ratios of surfactant to oil than conventional nonionic (or ionic surfactants with lipophilic coactives) aqueous or alcohol free compositions. As such, the present fragrance compositions are sprayable and nonsticky.</p>		

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- 1 -

Perfume formulations

5 This invention relates to the preparation of low VOC, aqueous or low ethanolic, clear, sprayable, non-sticky fragrance formulations containing conventional aroma chemicals at levels of 0.5% to 40%, preferably 1% to 30%, which are in a new microemulsion composition.

10 The need to have cosmetically acceptable, sprayable, low or zero ethanol fragrance formulations is due to concerns about volatile organic compounds (VOC), which are claimed to produce ground level ozone under certain extreme weather conditions. Fragrances at levels of 0.5% or above are most commonly solubilized with ethanol. However, ethanol is considered to be a VOC under many current and pending regulations.

15 The task of producing a low or zero ethanol formulation, which resembles an ethanolic fragrance formulation in all aspects, is difficult and the problem increases as the level of fragrance increases. Low ethanol formulations are formulations which are substantially free of ethanol.

20 Blakeway (Perfumer & Flavorist, 18, 23, 1993) reviews water based perfumes. He focuses on the use of solubilizers, in particular, non-ionic surface active agents. The formulations given by Blakeway require high ratios of surfactant to perfume oil which leave a sticky feeling on the skin and can produce unwanted levels of product foaming. At page 24, column 1, paragraph 3 Blakeway indicates that perfume compositions having 10% or greater perfume oils give viscosities of 20-50 cps which can not be used in conventional pump sprays. Also, higher concentrations of surfactants needed for the higher concentration of perfume oils gives the microemulsions their tendency to foam in the bottle. At page 26 under the heading "pump

- 2 -

spray" this document teaches that a viscosity of less than about 15 cps (conveniently at the ambient temperature, e.g. at 20°C) of a water based perfume is needed for pump spray applications. Viscosities of ca. ≤ 15 cps seem thus according to this author to be a characterising feature of
5 such sprayable, i.e. final compositions.

$$[1 \text{ cps} = \frac{1 \text{ g cm}^{-1}\text{s}^{-1}}{100} = 10^{-3} \text{ Pa.s} = 1 \text{ m Pa.s}].$$

Microemulsions represent one approach to producing clear,
10 transparent products. These are dispersions of oil-in-water or water-in-oil systems in which the droplet size is small enough to permit light to pass through. US patent 4,146,499 shows how oil-in-water microemulsions can be prepared using a primary surfactant with a hydrophilic-lipophilic balance ("HLB") not substantially less than
15 required to make it soluble in the oil phase. A second surfactant having a higher HLB than the primary surfactant, is used to convert the dispersion to a microemulsion. Non-ethanol fragrances produced by this method are viscous and translucent even at low, e.g., 1%, fragrance levels.

20

Linn et al., disclose in US patent 4,797,272, water-in-oil micro-emulsions for cosmetic uses containing moisturizing agents or sunscreens. These microemulsions are formulated with non-ionic surfactants and produce products comparable to typical skin care
25 creams and lotions and are not at all similar to perfume and cologne formulations. While some may be flowable, none is sprayable and non-tacky which are fundamental requirements for replacement of ethanolic perfume products.

30

U.S. Patent 5,252,555 (Dartnell et al.) (= EP Publication 516,508) relates to microemulsions containing a perfuming concentrate from 5 to 50% by weight, and a surfactant based on polyethylene glycol, a first co-surfactant based on polyglycerol and a second co-surfactant based on ether phosphate. Thus the compositions contain a very large amount of

- 3 -

surfactant. Moreover, the surfactants utilized in these compositions are non-ionic surfactants.

Microemulsions in which the primary surfactant is anionic have
5 been studied. However, coactives are required to modify the HLB and
allow the formation of microemulsions. This prior art (as discussed by
Friberg, et al, Cosmetics & Toiletries, Vol. 97, June 1982 and Kozo
Shinoda and Hironobu Kunieda in Microemulsions, Theory and
Practice, ed., Leon Prince, Academic Press, 1977) disclosed that a
10 lipophilic coactive, such as a medium chain length alcohol, is required
to reduce the HLB into the range required for microemulsion
formation. Use of these lipophilic coactives as the sole coactive at the
required levels for microemulsions, is not desirable for perfume
compositions because they typically have unpleasant odors and
15 frequently have undesirable skin feel characteristics.

U.S. Patent 4,146,499 (Rosano) teaches the use of two surfactants
to produce microemulsions, but does not produce sprayable
compositions at higher perfume oil concentrations. The non-ethanol
20 fragrances produced by this method are viscous and translucent even
at low, for example 1%, fragrance levels. The language in this patent
is very broad as regards a first surfactant which is lipophilic and a
second surfactant which is hydrophilic.

25 European Patent Publication 571,677 relates to clear oil-in-water
microemulsions comprising a perfume oil, an aqueous phase and a
surfactant. The microemulsions comprise less than 25%, preferably
less than 5% alcohol. The surfactants may be either ionic or non-ionic.
The co-surfactants are present in less than 50% by weight of the total
30 surfactant as described on page 5, lines 33-38. This reference does not
describe an anionic surfactant at a concentration lower than a coactive.
Further, the European patent application does not describe any
microemulsions comprising a perfume oil, an anionic surfactant in
combination with a hydrophilic coactive solvent, wherein the

- 4 -

hydrophilic coactive is in higher concentration than the anionic surfactant.

European Patent Publication 572,080 (Behan et al.) concerns
5 aqueous perfume oil micro-emulsions. The text of the patent
application is similar to the text of European Patent Publ. 571,677.
Example 3 shows a combination of primary nonionic surfactants plus
cosurfactants at least one of the cosurfactants being anionic. The
micro-emulsions are characterized as being fine fragrances or air
10 fresheners. The claim states that the weight ratio of perfume oil to total
surfactant is between 0.85 and 2.5, which stated in the reverse is that
the ratio of total surfactant to perfume oil is from about 0.4 to about 1.2.

Other background art is discussed below.

15

Japanese Kokai 161698/1993 (ST Chemicals Limited) relates to
water soluble solvents and water in combination with perfume oils.
Accordingly this document does not relate to perfume oils micro-
emulsified via an anionic surfactant in combination with a hydrophilic
20 coactive.

U.S. Patent 5,283,056 (Chung et al.) relates to mouthwash
compositions comprising water, a flavor or fragrance oil, and one or
more surfactants. As described on page 4, lines 50-55 the mouthwash
25 compositions have a viscosity ranging from about 70 to about 18,000 cps.

Japanese Kokai 57-159707 relates to solubilizing perfume oils in
water or an aqueous medium. A mono- or poly-hydric alcohol is used
in combination with a surfactant to solublize the perfume oils.

30

U.S. Patent 4,089,814 (Schmolka) relates to roll-on perfume
compositions comprising 25-40 parts of an alcohol and block copolymers
as well as water. A requirement for such compositions is that the
compositions are viscous, clear and stable perfumes. Clearly such
35 viscous compositions are not sprayable compositions. Further there is

- 5 -

no mention of an anionic surfactant in combination with a hydrophilic coactive.

EP 261,351 Publication (Blakeway) relates to aqueous or aqueous-
5 alcoholic solutions of fat soluble perfume oil containing an alkylene
oxide polymer and a nonionic emulsifier. Thus document does not
describe sprayable perfumes utilizing an anionic surfactant in
combination with a hydrophilic coactive.

10 U.S. Patent 4,268,498 (Gedeon et al.) relates to solid clear
cosmetic sticks. Thus, sprayable compositions are not described.
Although the compositions are described as clear they are also viscous
because they are in a solid stick form.

15 German Offenlegungsschrift 2901068 relates to deodorant
compositions. The composition is a clear solution comprising a large
amount of an anionic surfactant.

German Offenlegungsschrift 3304822 relates to an odorant
20 composition containing hexaalkyl-cyclo-trisiloxane perfume vehicles
which dissolve a perfume and sublimate into the environment carrying
the perfume into the air. Other volatile additives can be included to
reduce the sublimation rate. Therefore, this document does not
disclose a combination of an anionic surfactant and a coactive. The
25 carrier agent is non-ionic.

U.S. Patent 5,079,227 (Handjani et al.) relates to perfume
compositions, with an aqueous phase, having a high concentration of
perfume contained within nonionic lipid "vesicles." The lipid vesicles
30 are derived from a linear or branched polyglycerol. Such lipid vesicle
compositions are distinguished from oil-in-water or water-in-oil
emulsions by Handjani et al in their discussion of background art.
Further, the examples on pages 4-6 of Handjani et al refer to the
compositions as compositions having the appearance of a cream.

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- 6 -

U.S. Patent 4,810,690 (Dumas) relates to non-flammable homogeneous liquid air freshener compositions with an organic solvent base, which are not microemulsions of perfume oils.

- 5 UK Patent Publication 2,230,447 relates to solublized air freshener compositions, rather than to microemulsified perfume compositions. A primary alcohol is used to solubilize the perfume oil in the described compositions. A secondary low volatility solvent, such as a glycol ether is used to slow the evaporation of the alcohol solvent.
- 10 Thus the mechanism is not the formation of a clear microemulsion, but rather a homogeneous solution is formed.

- This present invention provides oil-in-water (O/W) and water-in-oil (W/O) microemulsion fragrance product formulations which are
- 15 (clear or at least translucent), sprayable, and non-sticky. In accordance with the invention, novel combinations of anionic surfactants and hydrophilic solvent coactives are used to obtain fragrance product formulations that are free or substantially free of ethanol. More particularly, the invention relates to the use of anionic
- 20 surfactants having an HLB which has been modified by the use of classes of (hydrophilic solvents) coactives not previously recognized as effective in this type of system.

- Surprisingly, it has been found that instead of lipophilic
- 25 coactives, certain hydrophilic highly, preferably infinitely, water soluble coactives (hydrophilic solvents) as well as mixtures of highly, preferably infinitely, water soluble solvent coactives with other less water soluble polar solvent coactives, modify the HLB of anionic surfactants. The HLB is sufficiently modified by the highly water-
- 30 soluble hydrophilic coactives, or mixture of highly water-soluble hydrophilic coactives and less water-soluble polar coactives, that stable, clear microemulsions of fragrance product compositions are able to be formed.

- 7 -

These compositions contain lower ratios of surfactant to oil than conventional nonionic aqueous or alcohol free compositions. Further, the amount by weight of hydrophilic solvent coactive, or mixture of coactives, by weight is greater than the amount of anionic surfactant in these fragrance compositions. As such, the fragrance compositions in accordance with the invention are sprayable and non-sticky.

The perfume materials are generally present in said formulations in amounts within the range of about 0.5% to 40%, preferably 1.0 to 30% by weight of the final formulation.

The primary surfactant, which is anionic, is typically present in levels of about 1.0% to 40%, preferably 2.0% to 20% by weight of the final formulation.

The hydrophilic coactive solvent is present in a level that exceeds that of the anionic surfactant. Typically, the hydrophilic coactive solvent is in the range of about 1.5% to 55%, preferably 6.0% to 45% by weight of the final formulation.

In the present invention, different levels of fragrance material are solubilized by a combination of an anionic component (a) and at least one hydrophilic component (b), wherein

(a) is an anionic surfactant or a combination of anionic surfactants, said surfactant or surfactants being selected from the group consisting of acyl glutamates, alkyl sulphates, alkali metal sulphates, ammonium sulphates, substituted ammonium alkyl sulphates, alkyl ether sulphates having 10 to 30 carbon atoms in the alkyl moiety and 1 to 50 ethylene oxide units, sulphosuccinates, alkyl sulphonates, alkyl oxyalkane sulphonates, alkyl aryl sulphonates, alkanolic acid, alkanolates, sodium alkanolate soaps wherein the fatty acid moiety contains 10 to 20 carbon atoms, potassium alkanolate soaps wherein the fatty acid moiety contains 10 to 20 carbon atoms, triethanolamine soaps wherein the fatty acid moiety contains 10 to 20 carbon atoms, and acyl isothionates, or a combination thereof; said

- 8 -

anionic surfactants being capable of forming a dispersion of said fragrance oil, or mixture of oils, and

(b) is a highly water soluble, or infinitely water soluble, hydrophilic coactive solvent or mixture of hydrophilic solvents, said
5 hydrophilic solvent or mixture being capable of sufficiently modifying the hydrophilic-lipophilic balance of said anionic surfactant or mixture of surfactants in said dispersion to enable formation of stable and clear, or near clear micro-emulsions of said fragrance oil or mixture of oils in water, said hydrophilic solvent or at least one of said
10 hydrophilic solvents, being selected from the group consisting of short branched-chain or straight-chain aliphatic glycols, short branched-chain or straight-chain aliphatic ether alcohols, and ethoxylated polysiloxanes;

15 wherein said hydrophilic component (b) is present at a higher concentration by weight than said anionic component (a) in said perfumery composition; and

wherein said fragrance oil, or mixture of fragrance oils, in
20 combination with said components (a) and (b) in said perfumery composition is/are microemulsified to clarity or near clarity in an aqueous solvent.

The resulting microemulsions, in addition to being stable and
25 clear or near clear, are also sprayable.

The fragrance materials of the perfumery compositions according to the invention are odiferous materials, which may be of any natural and/or synthetic origin. Of particular interest are oil soluble
30 perfume oils, which may or may not be in a mixture with water soluble perfume oils. The oil soluble perfume oils are natural, or nature-identical essential oils, such as orange oil, pine oil, peppermint oil, eucalyptus oil, lemon oil, clove leaf oil, cedarwood oil, bergamot oil, rosemary oil, patchouli oil, lavandin oil, spike oil, rose oil, vetiver oil,
35 fennel oil, anise oil, thyme oil, germanium oil, lavender oil, menthol

- 9 -

etc. The fragrance materials may also be synthetic oil soluble perfume oils, selected from the usual group consisting of hydrocarbons, alcohols, ketones, aldehydes, esters and polyene compounds, etc. Naturally, this term also encompasses any mixture of perfume oils
5 described above, or perfume concentrates or bases with preferably non-ethanolic diluents.

Preferred anionic surfactants (a) are selected from the group consisting of acyl glutamates such as monosodium cocoyl glutamate,
10 C₉₋₁₈ alkyl sulphates, sodium lauryl sulphate, sodium laureth sulphate, sodium dioctyl sulphosuccinate, sodium C₁₂₋₁₄ olefin sulphonate, sodium 2-methoxy-tridecanesulphonate, sodium dodecyl benzene sulphonate, potassium oleate, sodium caprylate, and sodium cocoyl isothionate, or a combination thereof. The acyl glutamates are
15 preferably C₁₂ to C₁₅ acyl glutamates.

Preferred highly water soluble, or infinitely water soluble, hydrophilic solvents (b) are selected from the group consisting of ethylene glycol, propylene glycol, butylene glycol, dipropylene glycol,
20 hexylene glycol, isoprene glycol, methyl methoxy butanol, ethylene glycol butyl ether, propylene glycol methyl ether, and dimethicone copolyol, or a combination thereof. A preferred dimethicone copolyol is Dow Corning 193TM.

25 Specifically, the compositions contain, primarily anionic surfactants component (a) at 1-40%, preferably 2-20%; component (b) at 1.5-55%, preferably 6-45%; which solublize perfume oils at levels of 0.5-40%, preferably 1-30%. The remainder of the formulation may be water or water/ethanol wherein the ethanol is present in only a low
30 concentration.

In another embodiment of perfumery compositions according to the invention, different levels of fragrance materials are solubilized by a combination of an anionic component (a) and at least one hydrophilic
35 component (b), wherein

- 10 -

- (a) is an anionic surfactant, or a combination of anionic surfactants, said surfactant or surfactants being selected from the group consisting of acyl glutamates, alkyl sulphates, alkali metal sulphates, ammonium sulphates, substituted ammonium alkyl sulphates, alkyl ether sulphates having 10 to 30 carbon atoms in the alkyl moiety and 1 to 50 ethylene oxide units, sulphosuccinates, alkyl sulphonates, alkyl oxyalkane sulphonates, alkyl aryl sulphonates, alkanolic acid, alkanooates, sodium alkanooate soaps wherein the fatty acid moiety contains 10 to 20 carbon atoms, potassium alkanooate soaps wherein the fatty acid moiety contains 10 to 20 carbon atoms, triethanolamine soaps wherein the fatty acid moiety contains 10 to 20 carbon atoms, and acyl isothionates, or a combination thereof; said anionic surfactants being capable of forming a dispersion of said fragrance oil, or mixture of oils, and
- (b) is a mixture of components (i) and (ii), wherein
- (i) is a highly water soluble solvent selected from the group consisting of short branched-chain or straight-chain aliphatic glycols, short branched-chain or straight-chain aliphatic ether alcohols, and ethoxylated polysiloxanes; and
- (ii) is a polar water soluble solvent selected from the group consisting of short branched-chain or straight-chain aliphatic alcohols, unsubstituted aromatic alcohols, aromatic alcohols substituted by a branched-chain or straight-chained alkyl group, aromatic ether alcohols, and dimethyl silicones terminated with hydroxyl groups;
- said mixture of (i) and (ii) being capable of sufficiently modifying the hydrophilic-lipophilic balance of said anionic surfactant or mixture of surfactants in said dispersion to enable formation of stable and clear, or near clear micro-emulsions of said fragrance oil or mixture of oils in water;
- wherein said hydrophilic component mixture (b) is present at a higher concentration by weight than said anionic component (a) in said perfumery composition; and

- 11 -

wherein said fragrance oil or mixture of fragrance oils in combination with said components (a) and (b) in said perfumery composition are microemulsified to clarity or near clarity in an aqueous solvent.

5

The fragrance materials of the perfumery compositions according to the invention are odiferous materials, which may be of any natural and/or synthetic origin. Of particular interest are oil soluble perfume oils, which may or may not be in a mixture with water soluble perfume oils. The oil soluble perfume oils are natural, or nature-
10 identical, essential oils such as orange oil, pine oil, peppermint oil, eucalyptus oil, lemon oil, clove leaf oil, cedarwood oil, bergamot oil, rosemary oil, patchouli oil, lavandin oil, spike oil, rose oil, vetiver oil, fennel oil, anise oil, thyme oil, germanium oil, lavender oil, menthol,
15 and the like, or combinations thereof. The fragrance materials may also be synthetic oil soluble perfume oils, selected from the usual group consisting of hydrocarbons, alcohols, ketones, aldehydes, esters and polyene compounds, and the like, or combinations thereof. Naturally, this term also encompasses any mixture of perfume oils described
20 above, or perfume concentrates or bases with preferably non-ethanolic diluents.

Preferred anionic surfactants (a) are selected from the group consisting of acyl glutamates such as monosodium cocoyl glutamate,
25 C₉₋₁₈ alkyl sulphates, sodium lauryl sulphate, sodium laureth sulphate, sodium dioctyl sulphosuccinate, sodium C₁₂₋₁₄ olefin sulphonate, sodium 2-methoxy-tridecanesulphonate, sodium dodecyl benzene sulphonate, potassium oleate, sodium caprylate, and sodium cocoyl isothionate, or combinations thereof.

30

Preferred highly water soluble, or infinitely water soluble, hydrophilic coactive solvents (i) are selected from the group consisting of ethylene glycol, propylene glycol, butylene glycol, dipropylene glycol, hexylene glycol, isoprene glycol, methyl methoxy butanol, ethylene
35 glycol butyl ether, propylene glycol methyl ether, and dimethicone

- 12 -

copolyol, or combinations thereof. A preferred dimethicone copolyol is Dow Corning 193™.

Preferred water soluble polar solvents (ii) are selected from the group consisting of hexanol, octanol, decanol, benzyl alcohol, phenyl ethyl alcohol, ethylene glycol monophenyl ether, and dimethiconol, or combinations thereof. Most preferred (ii) components are selected from the group consisting of aromatic components, e.g. benzyl alcohol, phenyl ethyl alcohol, and ethylene glycol monophenyl ether, the latter being especially preferred.

Specifically, the compositions contain, primarily anionic surfactants component (a) at 1-40%, preferably 2-20%; component (b) at 1.5-55%, preferably 6-45%; which solublize perfume oils at levels of 0.5-40%, preferably 1-30%. The remainder of the formulation may be water or water/ethanol wherein the ethanol is present in only a low, i.e. trace, concentration.

The anionic surfactants, or a combination of anionics, listed under component (a) are provided by way of example, but are not intended to be exhaustive of this class of anionic surfactants. Additional anionic surfactants which may be used are described in McCutcheon's Emulsifiers and Detergents, 1989, which is incorporated herein by reference. Some amphoteric surface active agents may also be present in the anionic surfactant component.

The listed highly, preferably infinitely, water soluble materials ((b) or (b)(i)), alone, or in combination, with less water soluble polar components (b)(ii), modify the HLB of the surfactant system to allow the formation of a clear microemulsion are merely non-exhaustive examples of a class of compounds. The (b), (b)(i), or (b)(ii) components, alone or in combination, may also function as antisticking and antifoaming agents.

- 13 -

Both the aqueous and oil phase of the microemulsion of perfumery materials may contain other ingredients such as emollients, silicones (e.g., polydimethyl siloxane and poly phenyl methyl siloxane), preservatives, vitamins, UV absorbers, buffers, colorants, opacifiers, or other ingredients known to those skilled in the art of formulating cosmetic products.

In the present invention it has been found that the use of anionics in combination with a greater quantity by weight of coactive hydrophilic component(s) having high water solubility, or a mixture of highly and less highly water soluble coactives, reduces the amount of surfactant (a) required to solublize the perfume in a given formulation. For example, as low as 2% surfactant (a), in combination with coactives ((b) or (b)(i) and (b)(ii)), can solublize 1% fragrance oil in a water base cologne. Further, 7% surfactant (a) together with coactives ((b) or (b)(i) and (b)(ii)) can solublize 40% of fragrance oil, or oils, in a perfume formulation.

Furthermore, the microemulsion compositions of the present invention provide superior skin feel and are sprayable as compared to compositions prepared with nonionic systems, or with ionic systems utilizing lipophilic coactives to modify the HLB.

These compositions may be used under warm, humid conditions in summer or under cold, dry conditions in winter. While stability is important from an esthetic point of view, the use of anionics helps to increase the operable range of microemulsions of the present invention.

In addition, since these formulations contain water, commercially available surfactant components (a) and commercially available hydrophilic component coactives ((b) or (b)(i) and (b)(ii)), they can be produced in a cost effective manner.

- 14 -

All examples which follow contain conventional perfumes consisting of natural and synthetic ingredients. Perfume concentrate E is a fragrance which is used in small amount in an after shower formulation, e.g. in a body splash. Four different perfume
5 concentrates F, H, K and L are used in a men's cologne. The four different perfume concentrates G, J, M and N are used in a women's cologne.

Preparation of the novel formulations is conveniently effected by
10 mixing the perfume concentrate with the coactive(s), preferably at room temperature, until a homogeneous mixture results and then adding the surfactant(s), with mixing until uniform. The resulting premix is titrated with water under vigorous stirring.

15 The following examples demonstrate the application of the present invention in a given formulation where relatively lower ratios of surfactant (a) compared to nonionic formulas are effective using a single highly soluble coactive component (b) or a combination thereof. All values are given in weight percent. Each of the resulting
20 compositions was sprayable, non-sticky and clear. It is also possible to include emollients or other typical cosmetic ingredients for consumer appeal.

Example 1

25

	A	B
Perfume E	1.0	1.0
Sodium lauryl sulfate	3.0	2.0
Dipropylene glycol	6.0	-
30 Dimethicone copolyol	-	6.0
Water to	100	100

- 15 -

Example 2

	Perfume J	37.5
	Sodium dioctyl sulphosuccinate	7.0
5	Dipropylene glycol	18.75
	Methyl methoxy butanol	18.75
	Water to	100.0

The following examples demonstrate formulations at multiple
 10 levels using mixtures of highly water soluble (i) and less water soluble
 (ii) coactives.

Example 3

15		A	B	C	D
	Perfume G	5.0	8.0	12.0	18.0
	Sodium lauryl sulphate	7.0	6.0	7.0	6.0
	Propylene glycol	7.5	20.0	18.0	20.0
	Ethylene glycol monophenyl				
20	ether	7.5	20.0	18.0	20.0
	Poly dimethyl siloxane	2.0	1.0	1.0	2.0
	Water to	100.0	100.0	100.0	100.0

In the above examples it can be seen that increasing levels of
 25 perfume can be solubilized with relatively low ratios of surfactant (a) to
 perfume by increasing the coactive component (b) Further
 formulations using mixtures of highly water soluble (i) and polar, less
 water soluble (b) coactive components are demonstrated below.

- 16 -

Example 4

	Perfume H	4.0
	Sodium cocoyl isothionate	4.0
5	Propylene glycol	25.0
	Ethylene glycol monophenyl ether	20.0
	Water to	100.0

Example 5

10	Perfume K	15.0
	Sodium caprylate	6.0
	Dipropylene glycol	47.0
	Decyl alcohol	7.0
15	Polyphenyl methyl siloxane	1.0
	Water to	100.0

Example 6

20	Perfume M	15.0
	Sodium lauryl sulphate	6.0
	Propylene glycol	34.0
	Ethylene glycol monophenyl ether	10.0
	Caproyl trimethicone	1.0
25	Water to	100.0

- 17 -

Example 7

	<u>A</u>	<u>B</u>
Perfume L	4.0%	--
5 Perfume F	--	3.0%
Sodium n-cocoyl L-glutamate	6.0%	5.0%
Hexylene glycol	10.0%	10.0%
Propylene glycol	10.0%	10.0%
Ethylene glycol monophenyl ether	10.0%	10.0%
10 Water to	100.0%	100.0%

Example 8

	<u>A</u>	<u>B</u>	<u>C</u>
15 Perfume N	10.0	10.0%	15.0%
Sodium n-cocoyl L-glutamate	7.0%	3.0%	7.0%
Sodium lauryl sulfate	--	3.0%	--
Hexylene glycol	10.0%	10.0%	9.0%
Propylene glycol	25.0%	25.0%	35.0%
20 Ethylene glycol monophenyl ether	10.0%	10.0%	9.0%
Water to	100.0%	100.0%	100.0%

To demonstrate the spectrum of perfume types that this microemulsion system can accommodate, model technical perfume blends were created as examples of (1) relatively water soluble mixtures and (2) relatively water insoluble mixtures.

Water Soluble Mixture (WS)

30 Diethyl malonate	20%
Linalool oxide	20%
Octahydro coumarin	20%
Phenyl ethanol	20%
Vanillin	20%

35

- 18 -

Water Insoluble Mixture (WI)

	Fixolide (1,1,2,4,4,7-hexamethyl-6-acetyl-1,2,3,4-tetrahydro-naphthalene)	20%
5	Hexyl cinnamic aldehyde	20%
	Iso E Super (1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethyl)-2-acetonaphthalin)	20%
	Lilial (p-tert.butyl- α -methylhydrocinnamic aldehyde)	20%
10	d-Limonene	20%

Example 9

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	
15	WS Perfume	5%	5%	15%	15%
	Sodium lauryl sulphate	6%	4%	6%	5%
	Propylene glycol	10%	20%	29%	32%
	Ethylene glycol monophenyl ether	-	5%	-	3%
	Water to	100%	100%	100%	100%

20

Example 10

	<u>A</u>	<u>B</u>
WI Perfume	5.0%	15.0%
25 Sodium lauryl sulphate	6.0%	5.0%
Propylene glycol	7.5%	25.0%
Ethylene glycol monophenyl ether	7.5%	20.0%
Water to	100.0%	100.0%

30 Obviously, combinations of water soluble and water insoluble formulations may be produced.

- 19 -

Example 11

	<u>A</u>	<u>B</u>
WS/WI @ 1:1	5%	15%
5 Sodium lauryl sulphate	6%	5%
Propylene glycol	16%	30%
Ethylene glycol monophenyl ether	5%	10%
Water to	100%	100%

10

Example 12

Each of the formulations in Examples 1-11 was tested for emulsion stability as follows. A sample of each formulation composition was subjected to at least three cycles of freezing and
15 thawing. After thawing the sample for at least the third time, the stability of the sample was checked. Each sample was still in the form of a sprayable emulsion. Thus, the formulations as described in Examples 1-11 are stable sprayable emulsions. Additionally, the formulations were subjected to standard stability testing at 40°F (4°C)
20 and 110°F (43°C) for 4 weeks.

The foregoing description has been provided for illustrative purposes. It will be recognized that variations on the inventive concepts disclosed herein may be envisioned which have not been
25 specifically enumerated above. Such variations are nevertheless intended to be encompassed within the scope of the invention as set forth in the following claims.

- 20 -

Claims

1. A low VOC, sprayable, non-sticky, non-ethanolic or low ethanolic, perfumery composition comprising a fragrance oil or a mixture of fragrance oils microemulsified by a combination of an anionic component (a) and at least one hydrophilic component (b), wherein

(a) is an anionic surfactant or a combination of anionic surfactants, selected from the group consisting of acyl glutamates, alkyl sulphates, alkali metal sulphates, ammonium sulphates, substituted ammonium alkyl sulphates, alkyl ether sulphates having 10 to 30 carbon atoms in the alkyl moiety and 1 to 50 ethylene oxide units, sulphosuccinates, alkyl sulphonates, alkyl oxyalkane sulphonates, alkyl aryl sulphonates, alkanolic acid, alkanooates, sodium alkanooate soaps wherein the fatty acid moiety contains 10 to 20 carbon atoms, potassium alkanooate soaps wherein the fatty acid moiety contains 10 to 20 carbon atoms, triethanolamine soaps wherein the fatty acid moiety contains 10 to 20 carbon atoms, and acyl isothionates, or a combination thereof, said anionic surfactants being capable of forming a dispersion of said fragrance oil, or mixture of oils, and

(b) is a highly water soluble, or infinitely water soluble, hydrophilic coactive solvent or mixture of hydrophilic coactive solvents, said hydrophilic coactive solvent or mixture being capable of sufficiently modifying the hydrophilic-lipophilic balance of said anionic surfactant or mixture of surfactants in said dispersion to enable formation of stable and clear, or near clear micro-emulsions of said fragrance oil or mixture of oils in water, said hydrophilic coactive solvent or at least one of said hydrophilic coactive solvents, being selected from the group consisting of short branched-chain or straight-chain aliphatic glycols, short branched-chain or straight-chain aliphatic ether alcohols, and ethoxylated polysiloxanes, or a combination thereof;

- 21 -

wherein said hydrophilic component (b) is present at a higher concentration by weight than said anionic component (a) in said perfumery composition; and

5 wherein said fragrance oil or mixture of fragrance oils in combination with said components (a) and (b) in said perfumery composition are microemulsified to clarity or near clarity in an aqueous solvent.

10 2. The fragrance composition according to claim 1, wherein the fragrance component is an odiferous natural or synthetic material selected from the group consisting of oil soluble perfume oils, oil soluble perfume oils in a mixture with water soluble perfume oils, wherein the oil soluble perfume oils are:

15 (aa) natural, or nature-identical, essential oils selected from the group consisting of an orange oil, pine oil, peppermint oil, eucalyptus oil, lemon oil, clove leaf oil, cedarwood oil, bergamot oil, rosemary oil, patchouli oil, lavandin oil, spike oil, rose oil, vetiver oil, fennel oil, anise oil, thyme oil, germanium oil, lavender oil, menthol, or a combination
20 thereof;

 (bb) synthetic oil soluble perfume oils selected from the group consisting of hydrocarbons, alcohols, ketones, aldehydes, esters and polyene compounds, or a combination thereof; or

 (cc) a mixture of (aa) and (bb).

25

 3. The fragrance composition according to claim 1 or 2, wherein said odiferous natural or synthetic material is a natural or synthetic perfume oil, a mixture of perfume oils, or a perfume concentrate or base, in a non-ethanolic diluent or diluents.

30

 4. The fragrance composition according to claim 1 or 2, wherein said anionic surfactants (a) are selected from the group consisting of monosodium cocoyl glutamate, C₉₋₁₈ alkyl sulphates, sodium lauryl sulphate, sodium laureth sulphate, sodium dioctyl sulphosuccinate,
35 sodium C₁₂₋₁₄ olefin sulphonate, sodium 2-methoxy-

- 22 -

tridecanesulphonate, sodium dodecyl benzene sulphonate, potassium oleate, sodium caprylate, and sodium cocoyl isothionate, or a combination thereof.

5 5. The fragrance composition according to claim 1 or 2, wherein the highly water soluble, or infinitely water soluble, hydrophilic coactive solvent or solvents (b) is selected from the group consisting of ethylene glycol, propylene glycol, butylene glycol, dipropylene glycol, hexylene glycol, isoprene glycol, methyl methoxy butanol, ethylene
10 glycol monophenyl ether, ethylene glycol butyl ether, propylene glycol methyl ether, and dimethicone copolyol, or a combination thereof.

 6. The fragrance formulation according to Claim 1 or 2, wherein the perfume materials are present at levels between 0.5% and 40% by
15 weight of the composition.

 7. The fragrance formulation according to Claim 6, wherein the perfume materials are present at levels between 1% and 30% by weight of the composition.
20

 8. The fragrance composition according to claim 1 or 2, wherein one or more anionic surfactants of component (a) is present in said composition at levels between about 1-40% by weight of the composition.

25 9. The fragrance composition according to claim 8, wherein one or more anionic surfactants of component (a) is present in said composition at levels between about 2-20% by weight of the composition.

 10. The fragrance composition according to claim 1 or 2,
30 wherein component (b) is one or more highly or infinitely water soluble components present in said composition at levels between about 1.5-55% by weight of the composition.

 11. The fragrance composition according to claim 10, wherein
35 component (b) is one or more highly or infinitely water soluble

- 23 -

components present in said composition at levels between about 6-45% by weight of the composition.

12. The fragrance composition according to claim 1 or 2,
5 wherein component (a) is present in said composition at levels between about 1-40% by weight of the composition, component (b) is present in said composition at levels between about 1.5-55% by weight of the composition, said fragrance component is present at levels between 0.5-50%, and the remainder of said composition by weight is water or a
10 water/ethanol mixture wherein said ethanol when present is in low concentration.

13. The fragrance composition according to claim 12, wherein component (a) is present in said composition at levels between about 2-
15 20% by weight of the composition, component (b) is present in said composition at levels between about 6-45% by weight of the composition, said fragrance component is present at levels between 1-30% by weight of the composition, and the remainder of said composition by weight is water or a water/ethanol mixture wherein said ethanol is present in a
20 low concentration.

14. The fragrance composition according to claim 12, wherein component (a) is present in said composition at about 2% by weight of the composition, and said fragrance component is present at about 1%
25 by weight of the composition.

15. The fragrance composition according to claim 14, wherein component (a) is present in said composition at about 7% by weight of the composition, and said fragrance component is present at about 40%
30 by weight of the composition.

16. The fragrance composition according to claim 1 or 2, wherein the alkyl sulphate is sodium lauryl sulphate.

- 24 -

17. The fragrance composition according to claim 1 or 2,
wherein the sulphosuccinate is sodium dioctyl sulphosuccinate.

18. The fragrance composition according to claim 1 or 2,
5 wherein the acyl isothionate is sodium cocoyl isothionate.

19. The fragrance composition according to claim 1 or 2,
wherein the alkanoate is sodium caprylate.

10 20. The fragrance composition according to any one of claims 1
to 19, wherein the acyl glutamate is monosodium cocoyl glutamate.

21. The fragrance composition according to claim 1, wherein the
short chain aliphatic glycol is selected from the group consisting of
15 ethylene glycol, propylene glycol, butylene glycol, dipropylene glycol,
hexylene glycol, isoprene glycol, or a combination thereof.

22. A fragrance composition according to claim 1, 2, 3 or 4,
comprising the surfactant/coactive systems

20

a) sodium lauryl sulfate, dipropylene glycol and dimethicone
copolyol, or

b) sodium lauryl sulfate, propylene glycol, ethylene glycol
25 monophenyl ether and polydimethyl siloxane, or

c) sodium cocoyl isothionate, propylene glycol and ethylene glycol
monophenyl ether, or

30 d) sodium dioctyl sulphosuccinate, dipropylene glycol and methyl
methoxy butanol, or

e) sodium caprylate, dipropylene glycol, decyl alcohol and
polyphenyl methyl siloxane.

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- 25 -

23. A low VOC, sprayable, non-sticky, non-ethanolic or low ethanolic, perfumery composition according to any one of claims 1 to 4, comprising a microemulsion of conventional perfumery materials, said composition having a fragrance oil or a mixture of fragrance oils
5 solublized by microemulsifying said oil or oils by a combination of an anionic component (a) and at least one hydrophilic component (b),
wherein

(a) is an anionic surfactant, or a combination of anionic surfactants, selected from the group consisting of acyl glutamates,
10 alkyl sulphates, alkali metal sulphates, ammonium sulphates, substituted ammonium alkyl sulphates, alkyl ether sulphates having 10 to 30 carbon atoms in the alkyl moiety and 1 to 50 ethylene oxide units, sulphosuccinates, alkyl sulphonates, alkyl oxyalkane sulphonates, alkyl aryl sulphonates, alkanolic acids, alkanooates,
15 sodium alkanooate soaps wherein the fatty acid moiety contains 10 to 20 carbon atoms, potassium alkanooate soaps wherein the fatty acid moiety contains 10 to 20 carbon atoms, triethanolamine soaps wherein the fatty acid moiety contains 10 to 20 carbon atoms, and acyl isothionates, or a combination thereof, said anionic surfactants being capable of forming
20 a dispersion of said fragrance oil, or mixture of oils, and

(b) is a mixture of components (i) and (ii), wherein

(i) is a highly water soluble solvent selected from the group consisting of short branched-chain or straight-chain aliphatic glycols, short branched-chain or straight-chain aliphatic ether alcohols, and
25 ethoxylated polysiloxanes, or a combination thereof; and

(ii) is a polar water soluble solvent selected from the group consisting of short branched-chain or straight-chain aliphatic alcohols, unsubstituted aromatic alcohols, aromatic alcohols substituted by a branched-chain or straight-chained alkyl group, aromatic ether
30 alcohols, and dimethyl silicones terminated with hydroxyl groups, or a combination thereof;

said mixture of (i) and (ii) being capable of sufficiently modifying the hydrophilic- lipophilic balance of said anionic surfactant, or mixture of surfactants, in said dispersion to enable formation of stable and clear,

- 26 -

or near clear, microemulsions of said fragrance oil, or mixture of oils, in water;

5 wherein said hydrophilic component mixture (b) is present at
a higher concentration by weight than said anionic component (a) in
said perfumery composition; and

10 wherein said fragrance oil or mixture of fragrance oils in
combination with said components (a) and (b) in said perfumery
composition are microemulsified to clarity, or near clarity, in an
aqueous solvent.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 94/03541

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/00 A61K7/46

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	EP,A,0 571 677 (UNILEVER) 1 December 1993 cited in the application see example 5a ---	1-4, 6-15,17, 23
A	EP,A,0 316 726 (COLGATE-PALMOLIVE) 24 May 1989 see the whole document ---	1-23
A	US,A,5 082 584 (LOTH ET AL.) 21 January 1992 see the whole document ---	1-23
A	EP,A,0 516 508 (YVES SAINT LAURENT PARFUMS) 2 December 1992 cited in the application see the whole document ---	1-23
	--- -/-	

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 553 661 (RHONE-POULENC SANTE) 26 April 1985 see the whole document -----	1-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 94/03541

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0571677	01-12-93	EP-A- 0572080 JP-A- 6040877 US-A- 5374614	01-12-93 15-02-94 20-12-94
EP-A-0316726	24-05-89	US-A- 5076954 AU-A- 2506288 US-A- 5108643	31-12-91 18-05-89 28-04-92
US-A-5082584	21-01-92	US-A- 5075026 AU-B- 597367 AU-A- 7313887 BE-A- 1001742 CA-A- 1302194 CH-A- 676854 DE-A- 3716526 DK-B- 168958 FR-A,B 2599046 GB-A,B 2190681 HK-A- 60094 LU-A- 86888 NL-A- 8701215 SE-A- 8702084 TR-A- 25009 US-A- 5076954	24-12-91 31-05-90 26-11-87 27-02-90 02-06-92 15-03-91 26-11-87 18-07-94 27-11-87 25-11-87 08-07-94 22-11-88 16-12-87 22-11-87 01-09-92 31-12-91
EP-A-0516508	02-12-92	FR-A- 2676924 US-A- 5252555	04-12-92 12-10-93
FR-A-2553661	26-04-85	NONE	

